

CARBON DIOXIDE (CO₂) DRY REFORMING OF GLYCEROL FOR HYDROGEN PRODUCTION USING Ni/La₂O₃ AND Co/La₂O₃

NURSOFIA BINTI MOHD YUNUS

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**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

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ABSTRACT

Converting glycerol, obtained from biodiesel industry via dry reforming is considered as a promising route to improve the economic viability of biodiesel industry. The objective of this research work is to synthesize, characterize and conduct the catalytic activity test of CO₂ glycerol dry reforming using Nickel (Ni) and Cobalt (Co) supported Lanthanum oxide (La₂O₃) as catalyst. In this research, Ni/La₂O₃ and Co/La₂O₃ were tested in a fixed bed reactor at 700 °C, 1 atm and CO₂: glycerol of 1:1. The catalysts were prepared by using wet impregnation method and characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Bruanauer-Emmett-Teller (BET) and Fourier-Transform infrared spectroscopy (FTIR). From the characterization analysis, the results revealed that Ni based supported by La₂O₃ have smaller metal crystallite size as compared to Co supported La₂O₃ due to highly-dispersed of La₂O₃ in the Ni catalyst. The surface morphology of 10 wt% Ni/La₂O₃ catalyst also shows some crystallite particles with small diameter covered the lanthanum oxides support consistent with XRD result. BET surface area measurement gives higher surface area, 28.29 m²/ g for 10 wt% Ni/La₂O₃ as compared to 10 wt% Co/La₂O₃ which gives 13.032 m²/ g. Reaction studies demonstrated that 10 wt% Ni/La₂O₃ gives the highest performance of hydrogen production and glycerol conversion as compared to calcined La₂O₃, 5 wt% Ni/La₂O₃, 15 wt% Ni/La₂O₃, and 10 wt% Co/La₂O₃ with the yield and conversion of 11.8 % and 18.6 % respectively. Excellence catalytic performance of 10 wt% Ni/La₂O₃ may attribute to high activity of 10 wt% Ni/La₂O₃ towards hydrogen rich gas and great stability. Besides, smaller metal crystallite size and larger surface area may also contribute to accessibility of active catalytic area.

ABSTRAK

Penghasilan hidrogen melalui gliserol, yang diperolehi daripada industri biodiesel melalui 'dry reforming' dianggap sebagai salah satu cara yang dapat meningkatkan ekonomi industri biodiesel. Objektif penyelidikan ini adalah untuk mensintesis, mencirikan dan menjalankan 'dry reforming' menggunakan Nikel (Ni) dan Kobalt (Co) yang disokong Lantanum oksida (La_2O_3) sebagai pemangkin. Dalam penyelidikan ini, Ni/ La_2O_3 dan Co/ La_2O_3 telah diuji dalam reaktor pada suhu 700 °C, 1 atm dan CO_2 : gliserol, 1: 1. Pemangkin disediakan dengan menggunakan kaedah 'wet-impregnation' dan dicirikan oleh X-ray belauan (XRD), Imbasan elektron mikroskop (SEM), Bruanauer-Emmett-Teller (BET) dan Fourier-Transform Inframerah Spektroskopi (FTIR). Daripada analisis tersebut, keputusan telah menunjukkan bahawa Ni/ La_2O_3 mempunyai saiz kristal yang lebih kecil berbanding Co/ La_2O_3 dan hal ini berlaku disebabkan penyebaran yang banyak terhadap La_2O_3 didalam pemangkin Ni. Permukaan morfologi 10% Ni/ La_2O_3 juga telah menunjukkan beberapa kewujudan kristal yang mempunyai diameter yang kecil menutupi permukaan La_2O_3 . BET analisis juga telah membuktikan bahawa kawasan permukaan 10 % Ni/ La_2O_3 adalah lebih tinggi (28.29 m^2/g) berbanding 10% Co/ La_2O_3 (13,032 m^2/g). Kajian tindak balas bagi penghasilan hidrogen dan penukaran gliserol menunjukkan bahawa 10% Ni/ La_2O_3 menghasilkan gas hidrogen yang tertinggi berbanding pemangkin yang lain iaitu 11.8% dan 18.6%. 10% Ni/ La_2O_3 telah berjaya menghasilkan gas hidrogen yang tertinggi adalah disebabkan prestasi yang baik terhadap penghasilan gas hidrogen dan juga kestabilan pemangkin yang tinggi. Selain itu, saiz kristal yang kecil dan kawasan permukaan pemangkin yang lebih besar juga telah menyumbang kepada akses kepada kawasan pemangkin aktif.

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LIST OF ABBREVIATIONS

Al_2O_3	Aluminium oxide
Ag	Argentium
CO_2	Carbon dioxide
CO	Carbon monoxide
cm	centimetre
Ce	Cerium
CeO_2	Cerium oxide
Co	Cobalt
Co_3O_4	Cobalt oxide
$^{\circ}C$	Degree celcius
CH_3O_8	Glycerol
X_{gly}	Glycerol conversion
g	gram
H_2	Hydrogen
S_{H2}	Hydrogen selectivity
Y_{H2}	Hydrogen yield
Ir	Iridium
Fe	Iron
K	Kelvin
kV	Kilovolts
La	Lanthanum
La_2O_3	Lanthanum oxide
MgO	Magnesium oxide
CH_4	Methane
μ	Micro
Ni	Nickel
NiO	Nickel oxide
N_2	Nitrogen
O_2	Oxygen
Pd	Palladium
%	Percent
Pt	Platinum
Rh	Rhodium
Ru	Ruthenium
Si	Silicon
SiO_2	Silicon oxide
S/C	Steam-to-carbon ratio
T	Temperature
TiO_2	Titanium oxide
wt	Weight
H_2O	Water
Zr	Zirconium

LIST OF ABBREVIATIONS

APR	Aqueous Phase Reforming
ATR	Auto-thermal Reforming
BET	Bruanauer-Emmett-Teller
DI	Deionized water
EU	European Union
FFA	Free fatty acid
FTIR	Fourier-Transform Infrared Spectroscopy
GC-MS	Gas chromatography-mass spectroscopy
HPLC	High-performance liquid chromatography
SEM	Scanning Electron Microscopy
TCD	Thermal conductivity detector
WGS	Water gas shift
XRD	X-Ray Diffraction
YSZ	yttria-stabilized zirconia

1 INTRODUCTION

1.1 Motivation and statement of problem

High energy demand nowadays has led to crucial energy shortage. Currently, most of energy demands is actually from fossil-based resources and burning of fossil fuels has caused negative impact to environment such as global warming (James and Dugle, 2011). In order to save our environment, concerns to replace fossil fuels have becoming more attention. Many researchers has investigated and explained the potential alternative to replace this conventional sources. Renewable energy has becoming an option to achieve sustain energy requirements for the future. Today, many researchers around the world are interested in the use of biomass as a renewable energy. Biomass is biological material produced by living organisms which is based on plant and animal material. It is an environmental friendly sources and appears as a good source for production of fuels and chemicals (Peres *et al.*, 2011). Figure 1-1 below shows a review by the European Union (EU) consumption of energy by sources in 2014. Based on Figure 1-1 below, natural gas, crude oil and solid fuels were still dominating resources of energy, which is accounted 48.6 % of total energy while the renewable energy dominating resources of energy about 20.3% of total energy.

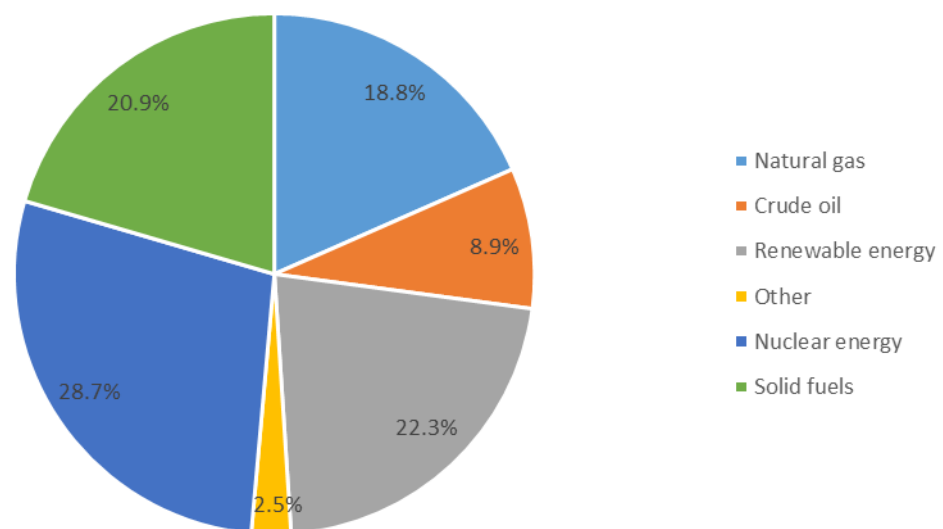


Figure 1-1: European Union (EU) consumption of energy by sources in year 2014

Biodiesel which is derived from biomass is one of the renewable resources and comparable to other alternative fuels. Biodiesel has major advantages and unique qualities as compared to petroleum diesel, since it is renewable and less polluting. Besides, it is also an oxygenated, sulphur-free and its content of oxygen could help to improve the combustion efficiency. In addition, it contributes much less to global warming than fossil fuels since carbon in the biodiesel are reused by the plants. Furthermore, biodiesel can increase engine life as it is more lubricating than diesel. Crude glycerol is one of the major by-products of biodiesel production. Crude glycerol can be refined into pure glycerol and then be used for cosmetic industries, pharmaceutical and food industries (Leoneti *et al.*, 2012). However, the purification process is too expensive to perform. Furthermore, according to Ahmed and Papadias (2010), as the production of biodiesel plant increased, market of pure glycerol will oversaturated and the price of crude glycerol will dropped as well. Silvey (2011) stated that biodiesel plant will have to pay to dispose the crude glycerol, instead of purifying and selling the crude glycerol. As a result, the production cost of biodiesel increases. Thus, finding out value-added chemical uses for this crude glycerol is aims to make the biodiesel production more cost effective.

Production of hydrogen or synthesis gas has becoming more popular nowadays especially in petroleum industries where hydrogen is used to remove sulphur from fuels. Besides, in chemical industries, hydrogen is used to produces chemicals such as ammonia, methanol and hydrochloric acid. In addition, hydrogen is very useful in industries like welding and metal fabrication and also food processing. Welding and metal fabrication use hydrogen to enhance plasma welding and cutting operations while food industries use the element to make hydrogenated vegetable oils such as butter and margarine. Conversion of glycerol to hydrogen is considered as a renewable alternative to reduce dependences on fossil fuels (Peres *et al.*, 2011). It can be performed by different process including pyrolysis, steam reforming, auto-thermal reforming, aqueous phase reforming and dry reforming which are recently studied by researchers worldwide (Lin, 2012).

Recently, steam reforming is the most widely process used in order to convert glycerol to hydrogen with the presences of catalyst. However, steam reforming is reported has side reactions which are methanation and carbon formation (Lin, 2012). On the other hand, dry reforming process offered a better pathway for the production of hydrogen.

Siew *et al.* (2013) reported that, dry reforming process is greener process that uses carbon dioxide as reactant and release water as by-products as compared to steam reforming. Furthermore, developing and improving the catalyst which can be operated at atmospheric pressure and producing higher amount of H₂ is considered to be more cost effective and environmental. Nickel (Ni) catalyst has been widely used in reforming process due to its low cost compared to noble metal catalyst such as platinum (Pt) and palladium (Pd) (Sabri, 2013). In order to make the economic feasibility of syngas production, the nickel catalyst is used with supported by oxides, such as La₂O₃. The good choice of supported material is important to avoid coke formation (Bermudez *et al.*, 2012). Till date, only a few researchers studies the dry reforming process by using nickel catalyst supported by oxides.

1.2 Objectives

The objective of this research are:

- To study feasibility of carbon dioxide (CO₂) glycerol dry reforming over nickel-supported lanthanum oxides and cobalt-supported lanthanum oxides.

1.3 Scope of this research

The following are the scope of this research:

- i) Synthesis of nickel-supported lanthanum oxides and cobalt-supported lanthanum oxides.
- ii) Characterization of catalyst to study the surface structure (SEM), specific surface area (BET) and crystalline structure (XRD), and functional groups (FTIR).
- iii) Reaction studies of CO₂ glycerol dry reforming using nickel-supported lanthanum oxide and cobalt-supported lanthanum oxide. Comparison has been made at different Ni loading (5 %, 10 %, 15 %) and cobalt loading (10 %). The reaction was carried out at fixed reaction condition.

1.4 Main contribution of this work

The following are the contributions of this work:

- Solving the economic challenge of biodiesel production by focusing on production of valuable products from crude glycerol and thus make biodiesel production more cost effective.
- Saving environment by finding the renewable alternative route to reduce dependences on fossil fuels for production of hydrogen.

1.5 Organisation of this thesis

The structure of each chapter of the thesis is outlined as follow:

Chapter 2 presents an overall of literature review that covering all aspects including the energy demands, biodiesel, glycerol, route of hydrogen production and catalyst. Detail studies on the dry reforming process is provided in this chapter. Besides, this chapter also gives an explanation about the process involving the crude glycerol as the by-product of biodiesel. A summary of the previous experimental work pyrolysis, steam reforming, aqueous phase reforming, auto-thermal reforming and dry reforming process are also presented. A brief discussion on catalysts is provided.

Chapter 3 gives a review on the synthesis technique of catalyst via co-wet impregnation method. This chapter also provides brief description on the characterization of catalyst via Brunauer-Emmet-Teller (BET), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR). A description on experimental work of CO₂ glycerol dry reforming over various type of metal-based catalysts supported on oxides are also presented. The analysis of the product was carried out using Gas Chromatography-Mass Spectrometry (GC-MS).

Chapter 4 discuss on the experimental results of catalyst characterization based on the catalyst morphology, surface composition and specific surface area. Preliminary studies on CO₂ glycerol dry reforming over nickel catalyst supported on lanthanum oxide were also discussed.

Chapter 5 draws together a summary of the thesis and presents the recommendations for the future work.

2 LITERATURE REVIEW

2.1 *Energy*

Energy comes from many sources and many forms such as light, heat, sound and motion. Energy sources can be classified into several groups which are non-renewable energy and renewable energy sources. Non-renewable energy source is energy that has limited supplies and extremely low to be regenerate includes natural gas, petroleum, coal, gasoline, diesel, propane, oil and petroleum products. Besides, non-renewable energy seems large and because of that, some experts believe that if the energy is used wisely, the energy supplies will be safe and long lasting for our future generations. Oil and diesel have becoming a good choices for fuels of vehicles. Furthermore, non-renewable energy has market value and enhancing economics. It can be used as bargaining tools to help economic stay afloat. However, there are many disadvantages of non-renewable energy. Burning of fossil fuels such as oil and diesel can contribute to global warming and pollution as it will produces carbon dioxide (CO₂) which is believe as a major causes of global warming to the earth.

On the other hand, a renewable energy source is energy that comes from a source that can be renewed. It is renewable, sustainable and never run out include wind energy, solar energy, methane, geothermal, hydroelectricity and biomass. Using renewable energy sources can give environmental advantage. This energy produce a little or no waste products such as carbon dioxide (CO₂) or other chemical pollutants that can give bad effects to the environment. Most of renewable energy produces no solid waste and reduces pollution too. This is because, solar energy, wind energy and hydroelectricity produce no emissions since none of renewable energy needs to be involve in burning process. Thus, using renewable energy did not contribute to greenhouse effect that link to global warming. Still, there are some disadvantages of renewable energy. Renewable energy often relies on the weather for its source of power. For examples, hydro generators need rain to fill dams to supply flowing turn blades and solar collectors need sunshine to collect heat to make electricity.

Today, global demand for energy has risen with industrial development and population growth. Energy is used among economic sectors such as residential, commercial,

transportation and industrial. Heating, cooling our homes, manufacturing of products and driving cars all require energy. Most of energy demand is actually from fossil-based resources. According to 2009 World Energy Outlook, which published by the International Energy Agency, world demand for oil will increase from 2000 million tons of oil to 16800 million tons of oil in 2030. Craving for energy is predicted continue rise, especially developing countries like China and India which seek the fuels for their rapid economic growth. However, burning fossil fuels will produce carbon dioxide and caused the increasing of greenhouse effect. Concerns are grown and focussed is also increase among researchers to replace fossil fuels in order to save environment. Finally, renewable options are necessary to achieve sustain energy requirements for future.

2.2 Synthesis Gas (Syngas)

The word syngas is derived from “synthesis gas” or producer gas, which is a gas mixture comprises of carbon monoxide (CO), hydrogen (H₂), and very often some carbon dioxide (CO₂). The name of synthesis gas is actually comes from its use as intermediate for production of ammonia or methanol. Besides, synthesis gas is a vital building block for the petrochemical industry and it is also used to prepare various chemicals (Lin, 2012). Synthesis gas is normally derived from a variety of different materials that contain carbon, such as natural gas or biomass.

Natural gas can be a reactants for production of bulk chemicals such as ammonia, methanol and dimethyl ether (Aasberg-Peterson *et al.*, 2011). According to Aasberg-Peterson *et al.* (2013), a method to convert natural gas to products is by synthesis gas with certain composition of reactants. For production of ammonia, the ratio is in range of 3:1 mixture of hydrogen and nitrogen while for production of dimethyl ether the ratio is in the range of 1:1 mixture of hydrogen and carbon dioxide. Besides that, catalyst and catalytic process is also important in synthesis gas using natural gas as a feedstock.

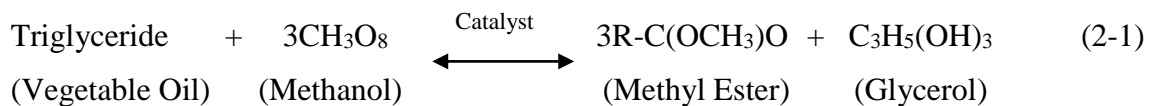
Today, many researchers around the world very interested in the use of biomass as a renewable energy. Source of biomass includes living organisms obtained from plant, trees or animal material. Examples of biomass are wood chips, corn, and left over food products like vegetable oils, animal fats that can produce biodiesel. The production of hydrogen or syngas is becoming one of popular process for biomass as a feedstock (Peres *et al.*, 2011). The production of syngas can be performed by different processes

such as pyrolysis, gasification and reforming. Reforming includes steam reforming, auto-thermal reforming, aqueous phase reforming and dry reforming which are recently studied by researcher worldwide (Peres *et al.*, 2011). In conclusion, syngas can be produced by using biomass as a feedstock in order to reduce dependences of fossil fuels.

2.3 Glycerol: Biodiesel By-product as a Feed of Glycerol Dry Reforming

2.3.1 Biodiesel

Biodiesel derived from biomass is renewable, abundant and one of the major sources for alternative fuels. Biodiesel is made from vegetable oil, animal oil or fats, waste cooking oil and algal oils by transesterification reactions in the presence of catalyst or without using catalyst. The transesterification process is the three steps reversible reaction of triglyceride (fat/oil) with an alcohol such methanol to form fatty acid methyl ester and glycerol. The general equation of transesterification reaction is shown in Eq. (2-1).



In biodiesel production process, oils with high free fatty acid (FFA) content will undergo pre-treatment for example esterification for reducing the FFA level of oil and then followed by transesterification reaction for converting fatty acid into fatty acid methyl ester. Transesterification reaction produce two layers of product after the settling process. The top phase is crude biodiesel while bottom phase is crude glycerol. Crude biodiesel were then refined in order to produce acceptable biodiesel for biodiesel industry. The article by Yang *et al.* (2012) described that, the increased biodiesel production will increased the production of crude glycerol as biodiesel production generated about 10 % (w/w) from total production of biodiesel as main by-products. This is also indicated that every gallons of biodiesel is actually generates approximately 1.05 pounds of crude glycerol (Yang *et al.*, 2012).

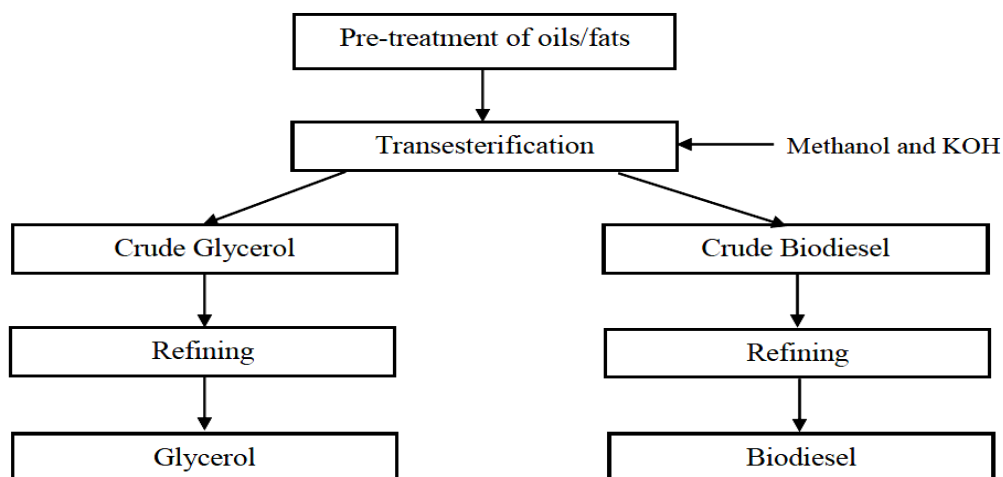


Figure 2-1: Illustration of the process flow diagram of biodiesel production process by Silvey (2011)

2.3.2 Glycerol

Glycerol, known as glycerine is trihydric alcohols which are colourless, odourless, sweet-tasting, syrupy liquid and one of the most widely available chemicals in the world. It is also useful chemicals with many applications. Its melting point is at 17.8 °C and boils with decomposition at 290 °C (Perry and Green, 1997). Lin (2012) stated that glycerol is classified as natural glycerol or synthetic glycerol. Natural glycerol can be derived from transesterification of biodiesel production and also through splitting of fats by saponification in the production of soap while synthetic glycerol can be derived from preparation of propylene oxide process. Based on report of Werpy *et al.* (2004), saponification is found as the major market supply for glycerol for a few last decades, however due to an increases of biodiesel production nowadays, glycerol produced from transesterification process was quite large as well (Pagliaro and Rossi, 2010).

From the biodiesel market overview, the world biodiesel market is expected to reach 37 billion gallons in 2016 (Yang *et al.*, 2012). As a result, the market of glycerol changes rapidly as biodiesel production becoming a global supply. Lin (2012) stated that, between 2010 and 2011, the price of glycerol in Asia market increases from US\$520 to US\$640 per tonne in the first quarter of the year and the latest prices of refined glycerol in 2012 were in range of US\$838 to US\$948 per tonne. This shows that, the prices of glycerol is increasing every year. However, Lin (2012) also stated that the price of glycerol, sometimes dropped in a certain year and this cause the price of glycerol is

difficult to be predicted for the future. According to Behr (2008), the large amount of glycerol derived by palm oil from countries like Malaysia and Indonesia which are the largest glycerol producers played a part in the price falling of glycerol to 33 cents per kilogram or less. Besides, most of companies produce glycerol have problem to purified and eliminate it due to its high cost. This has led the market of crude glycerol is swamp. Thus, biodiesel producers must find out value-added chemical uses for this glycerol to make the biodiesel production more cost effective.

2.3.3 Uses of Glycerol

There are three types of alternatives process that used crude glycerol as a feedstock which are purification, fermentation and synthesis gas process.

2.3.3.1 Purification

Crude glycerol can be refined into pure glycerol and then be used for cosmetic industries, pharmaceutical and food industries. However, it is too expensive to perform. Unrefined glycerol can be purified using distillation method. The crude glycerol obtained from biodiesel production contain a large amount of contaminants include fatty acid, soap, methanol and other degraded glycerine products. Therefore, purification of crude glycerol by vacuum distillation has to be done to prevent degeneration of glycerine (Xiao *et al.*, 2013). Although vacuum distillation is widely used for purifying glycerine to prevent degeneration of glycerine, the investment cost of vacuum distillation unit is not reasonable for small to medium-scale biodiesel producers. This can cause the production cost of biodiesel increases. Then, according to Ahmed and Papadias (2010), as the production of biodiesel plant increased, market of pure glycerol will oversaturated and the price of crude glycerol will dropped as well. Thus, instead of purifying and selling the crude glycerol, biodiesel plant will have to pay to disposed it (Silvey, 2011). In order to find alternatives ways to make biodiesel production more cost effective and reliable it is important to find out the market for this crude glycerol.

2.3.3.2 Fermentation

Crude glycerol derived from biodiesel production can become a feedstock in fermentation process for the production of chemicals such as lactic acid and citric acid. Lactic acid is very useful in food and beverage sector as a preservative and pH adjusting agent. It is used in the pharmaceutical and chemical industries, as a solvent and starting material in the production of lactate ester. Besides that, lactic acid is also used as active

ingredient in personal care products such as moisturising, pH regulating and skin lightening properties. In order to solve biodiesel cost issue, glycerol can be used as carbon source for production of lactic acid using pellet-form fungus *Rhizopus oryzae* NRRL 395. Vodnar *et al.* (2013) have studied on lactic acid production using pellet-form *Rhizopus oryzae* NRRL 395 on biodiesel crude glycerol. They had used fed-batch fermentation with crude glycerol, inorganic nutrients and lucerne green juice for the process. In their studies, they found out the growth of fungal is good on crude glycerol at 75 g l⁻¹ concentration with lucerne green juice supplementation of 25 g⁻¹ and it also can be conclude that amount of crude glycerol and lucerne green juice affect the L (+)-lactic acid production. Besides, citric acid also has been used widely as flavouring agent and is found in everything from candies and soda. It is also useful as an environmental cleaning agent and antioxidant. In industrial application, citric acid is widely used for making detergents while in pharmaceutical industry, citric is used as flavouring and stabilizing agent in pharmaceutical preparations. Rywinska *et al.* (2009) conducted the study on production of citric acid using acetate-negative mutants of *Yarrowia lipolytica* with crude glycerol in fed-batch fermentation. The yield of the product were the highest when *Y. lipolytica* Wrastrislovia AWG7 strain was used in the culture with crude glycerol. Furthermore, with a medium containing 200 g/l of glycerol, production of citric acid reached a maximum of citric acid which is about 139 g/l after 120 hours.

2.3.3.3 Synthesis Gas (Reforming)

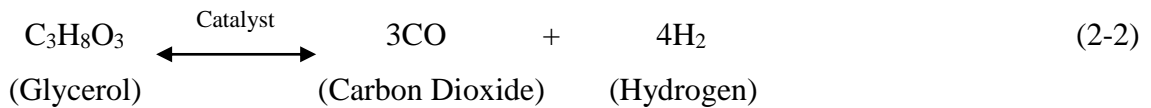
Production of hydrogen which is also known as synthesis gas is a viable alternative to improve economic viability of biodiesel industry and to increase the use of crude glycerol. Hydrogen is clean energy source with many uses and expected to increases in the future. In petroleum industries, hydrogen is used in order to remove sulphur while in chemical industries, hydrogen is used to produces chemicals such as ammonia, methanol and hydrochloric acid. Hydrogen is very useful in metal refining, food processing and electronic manufacturing. Food industries use hydrogen to make hydrogenated vegetable oils such as butter and margarine and welding companies use hydrogen for welding torches for steel melting. Converting glycerol to hydrogen is also considered as a renewable alternative to reduce dependences on fossil fuels (Peres *et al.*, 2011). There are several processes available for hydrogen and synthesis gas production include pyrolysis, steam reforming, auto-thermal reforming, aqueous phase reforming

and dry reforming (Lin, 2012). All these processes use crude glycerol as a feedstock for synthesis gas production.

2.4 Process Routes for Glycerol Reforming

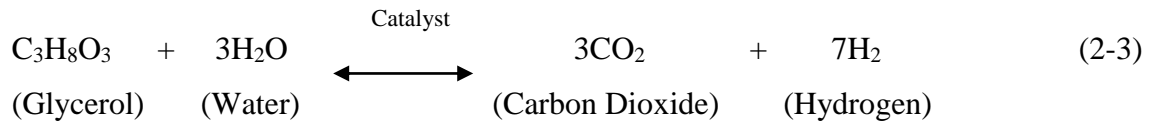
2.4.1 Pyrolysis

Pyrolysis is the process which can be done in two conditions, one is the catalyzed pyrolysis and another one is catalytic fast pyrolysis (Peres *et al.*, 2013). Pyrolysis is a simple process and cheap method for energy conversion. Glycerol pyrolysis is also a thermal decomposition process which occurs in the absence of oxygen. The process is highly endothermic (Lin, 2012). This process also has high thermal efficiency, short residence time and low CO₂ emission. There are two pathways involved for glycerol pyrolysis, one with the presence of carrier gas and another one without the carrier gas. Both processes produced hydrogen in a fixed bed reactor. According to Chaudhari and Bakhshi (2002), they ran the pyrolysis process at 400°C and 500°C with a flow rate of approximately 2 g/h. However, it was reported that the operation was quite difficult without using carrier gas because of disposable solid waste (char) formation in the feed inlet. The glycerol pyrolysis reaction is shown in Eq. (2-2).



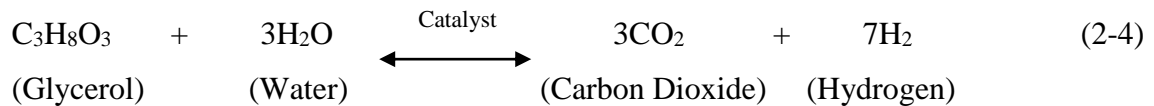
2.4.2 Steam Reforming

The process of steam reforming is the most widely used to convert glycerol to hydrogen with the presence of catalyst. According to Adhikari *et al.* (2009), in steam reforming process, the substrate is reacted with steam in the presence of a catalyst to generate hydrogen, carbon dioxide and carbon monoxide. The process is highly endothermic and low pressure favours the selectivity to hydrogen. The steam reforming process involves a combination of glycerol pyrolysis with water-gas shift reaction (i.e. reaction of water with carbon monoxide) (Lin, 2012). However, steam reforming is reported to have side reactions which are methanation and carbon formation (Lin, 2012). On the other hand, Cheng (2011) analysed that the steam reforming process is a mature technique which does not involve any complex control instrument. The equation for this process is shown in Eq. (2-3).



2.4.3 Aqueous Phase Reforming

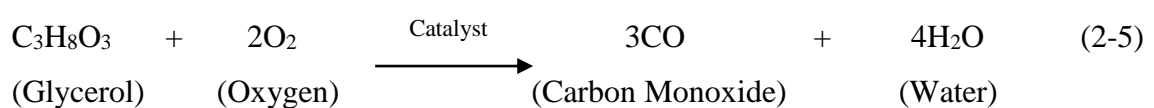
APR is a gasification process that transform glycerol in an aqueous phase without the pre-vaporization (Davda *et al.*, 2002). Step is performed in liquid phase under moderate temperatures and pressures. The products of this process are hydrogen and carbon dioxide. According to Cheng (2011), aqueous phase reforming can utilize low grade purity glycerol as reactant and occurs at temperature below than 573 K in single reaction. In addition, hydrogen can be extracted and purified from product stream of CO₂ and H₂ using pressure swing adsorption technology. Overall reaction of aqueous phase reforming is shown in Eq. (2-4).



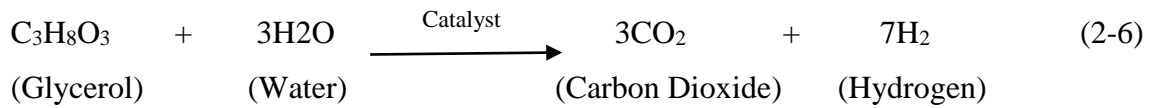
2.4.4 Auto-thermal Reforming (ATR)

Glycerol also can be converted to hydrogen via auto-thermal reforming (ATR) process. ATR process is the combination of steam reforming and partial oxidation effects by feeding fuel, air, and water together into reactor with the presence of catalyst. The products of this reaction are carbon monoxide, carbon dioxide and hydrogen. Partial oxidation process generates heat that can be utilized in the steam reforming process. Davenhauer *et al.* (2006) have studied ATR to produce hydrogen via glycerol. The process is actually not requiring any energy for reaction to take place. However, the amount of H₂ generated from the ATR process would be less based on thermodynamic studies (Sabri, 2013). They are four reactions involve for this process which are shown in Eq. (2-5), Eq. (2-6), Eq. (2-7), and Eq. (2-8).

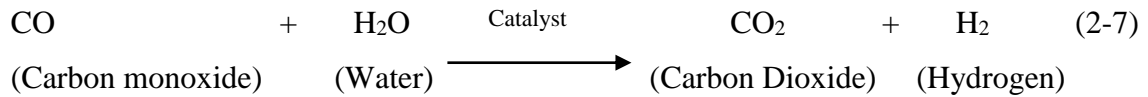
Partial oxidation:



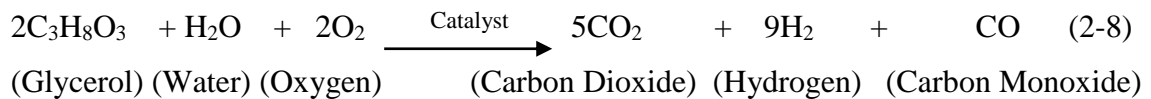
Parallel steam reforming of glycerol:



Series water-gas shift reaction:



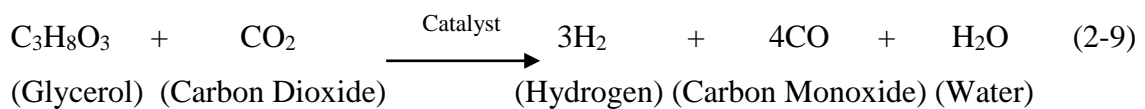
Overall reaction:



2.4.5 Dry Reforming

Dry reforming process is a greener process and one of alternative route for syngas production. In this process, the parameters that commonly being investigate are reaction temperature, pressure, residence time, catalyst loading and carbon dioxide-to-glycerol ratio. This process also believed to offer a better pathway for glycerol reforming (Siew *et al.*, 2013). Dry reforming process used glycerol and carbon dioxide as reactants and produce hydrogen, water and carbon monoxide as by-products.

Dry reforming of glycerol for synthesis gas production reaction:



Lee *et al.* (2013), studied the dry reforming of glycerol using Ni-catalyst support as catalyst. He developed cement clinker which comprised of 62% of calcium oxide supported nickel catalyst with metal loadings of 5, 10, 15 and 20 wt%. In this research, the reaction were conducted at 1023 K and they found that the H₂ and CO ratios

obtained is less than 2. Siew *et al.* (2013) also conducted glycerol dry reforming process over alumina (Al_2O_3) with non-promoted and lanthanum-promoted Ni catalysts. The experiment was carried out at 873 K and it was reported that 2 wt% La-Ni/ Al_2O_3 gave the highest H_2 yield compared to other catalysts. Besides, 5 wt% La-doped catalyst also showed poor performance due to excessive doping of La which resulted by encapsulation of available active sites. In another work, Wang *et al.* (2009) has conducted glycerol dry reforming and it was reported that, atmospheric pressure is preferable for this process with the conversion of glycerol yielded to 100%. According to same group of researchers, synthesis gas production via dry reforming able to produce 6.4 moles of syngas per mole of glycerol.

2.5 Catalyst

Catalyst plays an important role in glycerol dry reforming and mainly used to increase the reaction rate, increase the hydrogen selectivity and decrease the coke formation. The most important factor that need to be focussed on selecting the best catalyst for this process is the ability of catalyst to successfully reform glycerol. Most of studies have focussed on steam reforming process and very few studies have been performed on dry reforming process. According to Silvey (2011), it is important to select the best catalyst based on high order of reactivity level. For steam reforming process, the order of reactivity level of catalyst is (Ruthenium) Ru \approx Rhodium (Rh) > Nickel (Ni) > Iridium (Ir) > Cobalt (Co) > Platinum (Pt) > Palladium (Pd) > Iron (Fe) (Hirai *et al.*, 2005). A good catalyst should have high activity for C-C and O-H bond cleavage. Good reforming catalyst are mostly from group VIII transition metals which have excellence properties of tensile strength and rigidity includes Pt, Pd, Ni, Ir, Ru, Fe and Co (Davda, 2005). Cobalt is a non-noble metal which is widely used in reforming process. As outlined by Llorco, (2002), Song, (2007), and Moura, (2012), cobalt catalyst has been discovered to provide similar activity to noble metal catalysts in the C-C bond cleavage even at low temperature. This has been proved by Zhang *et al.*, (2007) where they revealed that Co-supported CeO_2 was active in glycerol steam reforming process as resulting complete glycerol conversion and 88 % hydrogen selectivity with low values of Co and CH_4 .

Noble metal catalysts such as Pt and Pd plays a crucial role in the production of hydrogen. However, many researchers indicates that, Pt and Pd are effective catalyst,

but there are very expensive. This can increase the production cost of hydrogen. The usage of base metal catalyst, such as nickel is thousand times less expensive than Pt and Pd. Nickel has most widely used catalyst in steam reforming process and also in dry reforming process for production of hydrogen. Nickel has high activity for C-C and O-H bond cleavage. Also, nickel is successful at making H atoms bond to form molecular H_2 , because it has hydrogenation. Moreover, Ni catalyst able to make production of hydrogen from glycerol more cost effective due to its low cost.

Still, Ni catalyst also undergo severe deactivation due to coke formation. Pakhare and Spivey (2014), have studied on dry reforming of methane over noble metal catalyst and they found that noble metal catalysts are typically found to be much more resistant to carbon deposition than Ni catalysts, but are expensive compared to Ni catalyst. Hence, developing and improving the catalyst which can increases hydrogen production is very necessary. For this present study, nickel and cobalt are decided to be used and tested in glycerol dry reforming process. In order to increases the economic feasibility of synthesis gas production, the nickel and cobalt catalyst is used with supported by oxides to avoid carbon deposition. The suitable choice of supported material and promoter is important to avoid coke formation. Table 2-1 and Table 2-2 below shows the catalysis studies in glycerol reforming process that have been studied before.

Table 2-1: Glycerol reforming process over Ni-based catalyst supported by oxides

Entry	Process	Active Phase	Support	T(K)	S/C ratio	Space Velocity	X glycerol (%)	S _{H2} or Y _{H2} (%)	Reference
1	Steam Reforming	Ni	TiO ₂ , MgO, CeO ₂	873	4	N.c.	60-100	S _{H2} = 28-75	Adhikari <i>et al.</i> (2008)
2	Aqueous Phase Reforming and Steam Reforming	Ni	Mg, Zr, Ce, or La-doped Al ₂ O ₃	873	33	2.5 h ⁻¹	100	S _{H2} = 60-70	Iriondo <i>et al.</i> (2008)
3	Steam Gasification	Ni	Al ₂ O ₃	1073	0-0.3	1.35-5.4 h ⁻¹	100	S _{H2} > 90	Valliyappan <i>et al.</i> (2008)
4	Steam Reforming	Ni	Al ₂ O ₃	673-973	3	1.5 × 10 ³ mL gcat ⁻¹ h ⁻¹	60-100	S _{H2} = 40-80	Dou <i>et al.</i> (2009)
5	Steam Reforming	Ni	CeO ₂ , Al ₂ O ₃ , and Ce-doped Al ₂ O ₃	773-873	46	7.7 h ⁻¹	25-100	Y _{H2} = 30-90	Iriondo <i>et al.</i> (2010)
6	Steam Reforming	Ni	ZrO ₂	850-923	2-3	1.5 × 10 ³ h ⁻¹	100	S _{H2} = 64-95	Wang <i>et al.</i> (2010)
7	Steam Reforming	Ni	Al ₂ O ₃	723-823	1.1-4	1.5 × 10 ⁴ – 4.2 × 10 ³ mL gcat ⁻¹ h ⁻¹	54.2-79.8	S _{H2} = 92-137	Cheng <i>et al.</i> (2011)
8	Steam Reforming	Ni	γ- Al ₂ O ₃	873	8	1.8 × 10 ³ mL gcat ⁻¹ h ⁻¹	70-100	Y _{H2} > 90	Choi <i>et al.</i> (2011)
9	Dry Reforming	Ni	Cement clinker	1023	N.c.	3.6 × 10 ⁴ mL gcat ⁻¹ h ⁻¹	46-76	Y _{H2} = 29-66	Lee <i>et al.</i> (2014)
10	Dry Reforming	Ni	La-doped Al ₂ O ₃	873	N.c.	3.6 × 10 ⁴ mL gcat ⁻¹ h ⁻¹	<96	Y _{H2} < 2.0	Siew <i>et al.</i> (2015)

N.c.: not communicated. X glycerol (%): glycerol conversion. S/C ratio: steam-to-carbon ratio. Y_{H2}: H₂ yield. S_{H2}: H₂ selectivity